REPORT DOCUMENTATION PAGE

AFRL-SR-BL-TR-98-0054

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
		Fjinal 01 Aug 93 to 31 Jul 97

4. TITLE AND SUBTITLE
(Asert-93) Electorn impact ionization and dissocation of molecules used in plasma etching and deposition of semiconductors

5. FUNDING NUMBERS
61103D
3484/TS

6. AUTHOR(S)
Professor McKoy

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
California Institute of Technology
Sponsored Research
Mail Stop 213-6
Pasadena CA 91125

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NE
110 Duncan Ave Room B115
Bolling AFB DC 20332-8050

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
F49620-93-1-0438

11. SUPPLEMENTARY NOTES

19980116 037

12a. DISTRIBUTION/AVAILABILITY STATEMENT

APPROVAL FOR PUBLIC RELEASED: DISTRIBUTION UNLIMITED

Abstract

Cross sections for electron-impact dissociation of molecules are essential to improved modelling of the plasmas used in microelectronics fabrication. The available data on such cross sections for gases of interest in plasma processing is, however, very fragmentary and, furthermore, measurements of these cross sections for dissociation into neutral fragments is very challenging. While computational approaches to obtaining these data are thus clearly of value, calculations of electron-molecule collision are difficult at the low energies of interest and progress has been quite limited.

In this project we have developed innovative scalable implementations of our theory of electron collisions which have made it possible to harness the computational power of the largest parallel computers to obtain electron-collision cross sections needed in modelling plasmas used in semiconductor fabrication. We have successfully exploited these algorithms and parallel computer resources to study such cross sections for gases such as CHF_3, C_2F_6, C_3F_8, c-C_4F_8, PH_3, AsH_3, and $BC\ell_3$.

OF REPORT	OF THIS PAGE	OF ABSTRACT	
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

Final Technical Report

AFOSR Grant No. F49620-92-J-0438

Electron-Impact Dissociation of Molecules Used in Plasma Etching and Deposition of Semiconductors

Principal Investigator: Vincent McKoy

Performance Period: Aug.1, 1993- July 31, 1997

Attn.: Dr. Ralph Kelley
AFOSR
Bolling AFB
Phone: 202-767-4984

Abstract

Cross sections for electron-impact dissociation of molecules are essential to improved modelling of the plasmas used in microelectronics fabrication. The available data on such cross sections for gases of interest in plasma processing is, however, very fragmentary and, furthermore, measurements of these cross sections for dissociation into neutral fragments is very challenging. While computational approaches to obtaining these data are thus clearly of value, calculations of electron-molecule collision are difficult at the low energies of interest and progress has been quite limited.

In this project we have developed innovative scalable implementations of our theory of electron collisions which have made it possible to harness the computational power of the largest parallel computers to obtain electron-collision cross sections needed in modelling plasmas used in semiconductor fabrication. We have successfully exploited these algorithms and parallel computer resources to study such cross sections for gases such as CHF_3, C_2F_6, C_3F_8, c-C_4F_8, PH_3, AsH_3, and $BC\ell_3$.

I. *Background and Objectives*

Cross sections for electron-impact dissociation of molecules play an important role in determining the properties of the materials-processing plasmas used in microelectronics fabrication. In fact, plasma etching, plasma deposition, and several other plasma-based processes are at the foundation of the microelectronics industry. The data base of these electron-collision cross sections for species arising in plasmas of interest is very fragmentary and often non-existent. Furthermore, measurements of electron-impact dissociation of molecules into ground state fragments are very limited and challenging due to difficulties in detecting such fragments. Electron-impact dissociation cross sections are especially important in modelling these plasmas since these collisions are the principal mechanism for generating reactive species in these plasmas.

Calculations of electron-molecule collisions are also difficult at the low energies of interest. Thus, although the physical principles in low-energy electron-molecule collisions are well understood, and although several methods have been developed for numerical studies of these collisions, progress in their application has been limited. What is required is not just a method and algorithm by which the problem might be solved in principle, but an *implementation that makes relevant problems feasible.* The thrust of our effort has been to develop innovative scalable implementations of our theory of electron collisions[1] – the Schwinger multichannel variational method – with which we could harness the computational power of large parallel computers to obtain electron-collision cross sections needed in modelling plasmas that are widely used in semiconductor fabrication.

II *Technical Summary*

Plasma reactors are used in 30 to 40% of the processing steps in semiconductor fabrication. The cost of such semiconductor fabrication facilities is escalating, as is the research and development cost of introducing each new generation of plasma processing technology. It is now recognized that comprehensive three-dimensional, time-dependent simulations of these plasma reactors are essential to reducing the need for the costly and time-consuming experimental characterization currently required to develop a new generation of processing equipment. While such simulations have generally been beyond the reach of conventional supercomputers, large-scale parallel computers now have the potential to make them possible with industrially viable turnaround times.

While improved simulations of plasma reactors will depend on the availability of basic data for many processes in the plasma and at the surface, data for electron-molecule

collisions, a principal mechanism for generating useful reactive species in these plasmas, are, however, especially important. As for many other processes in these plasmas, there are large gaps in the electron-collision data for gases of interest in microelectronics fabrication. Furthermore, cross sections for electron-impact dissociation of molecules into neutral fragments are among the most difficult to measure, many feed gases are hazardous, and transient fragments produced in situ may be experimentally inaccessible.

Computational approaches to obtaining such data are thus potentially of significant value. The collision of low-energy electrons with molecules is, however, a complex quantum mechanical problem. Calculating the probabilities of various possible outcomes of such a collision – that is, the scattering cross sections – is a correspondingly computationally intensive challenge. Hence, while several methods have been developed for numerical studies of such collisions, progress in their application to polyatomic gases of interest to plasma processing, e.g., species containing several carbon and halogen atoms, has been very limited. What is necessary to address this need in simulations of these plasmas for electron-collision cross section sets for multiple species is obviously a method of sufficient accuracy that is nonetheless computationally feasible for polyatomic feed gases.

In this effort we have exploited large-scale parallel computers, consisting of hundreds of microprocessors, to generate electron-collision cross section data for gases of interest in plasma simulations. In these studies we employ a parallel adaptation of a computational procedure based on a multichannel variational procedure which we specifically developed for studying low-energy electron-molecule collisions.[1] Like most variational schemes, the computational problem reduces to a set of linear equations – in matrix form, finding the unknown matrix $\mathbf{x}$ in the equation $\mathbf{A}\ \mathbf{x} = \mathbf{b}$. It is constructing, not solving, the linear system that is the computationally challenging part of our calculation.

Construction of this $\mathbf{A}$ matrix requires a quadrature approximation to an integral operator associated with the free-particle Green's function, which arises due to the boundary condition requirements of the collision. Since this quadrature is carried out over an infinite three-dimensional domain, tens of thousands of quadrature points may be required. At each quadrature point, we must evaluate all possible six-dimensional integrals of the form

$$\int\int d^3r_1\ d^3r_2 \frac{F_a(\mathbf{r}_1)F_b(\mathbf{r}_1)F_c(\mathbf{r}_2)\exp(i\mathbf{k}\cdot\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} \tag{1}$$

Here, F_a, F_b, and F_c are Cartesian Gaussian functions, which are familiar to quantum chemists, and k is the quadrature variable. There are about $G^3/2$ unique ways to choose the indices a, b, and c given a set of G Gaussians, so for G around 200 (typical in our work) we may need to evaluate as many as a few million such integrals at each of the quadrature

points in $\mathbf{k}$. A large number of integrals ($\sim 10^9 - 10^{11}$) might hence be required in a cross section calculation.

Fortunately, the integrals in (1) can be evaluated analytically. This is no coincidence: Gaussians are used precisely because the resulting integrals are doable. Any single integral may therefore be obtained with little computational effort; what makes the problem numerically intensive is the vast number of integrals involved. However, it is not just evaluating all these integrals that is demanding. There are several intermediate steps in the process of building the elements of $\mathbf{A}$ and $\mathbf{b}$ from the integrals in (1), and the arithmetic associated with these steps often involves more operations than the actual computation of the integrals.

The outline of the numerical procedure is now obvious: first, evaluate a large number of integrals of the type shown in (1); next, combine those integrals in appropriate ways to construct matrices $\mathbf{A}$ and $\mathbf{b}$; finally, solve the resulting linear system. It is obvious that at least the first step in this procedure – evaluating a batch of integrals – is well suited to distributed-memory parallel machines such as the *Intel Paragon* and *Cray T3D*: We simply assign each processor a different subset of integrals to evaluate. Combining the integrals is more challenging, since the rules for building elements of $\mathbf{A}$ and $\mathbf{b}$ from the integrals are fairly complicated and the processors must communicate with each other in this phase (because each processor has only a fraction of the current batch of integrals in its own memory). An efficient way of carrying out this step is to use the complicated rules for combining integrals to build a single transformation matrix that, when multiplied with the current batch of integrals (arranged as a matrix) gives the necessary combination as a product matrix.[2] Each processor can build a block of this transformation matrix independently, so that the only communication among processors occurs during the matrix multiplication. A subsequent step in evaluating $\mathbf{A}$ – namely, the angular part of the quadrature over $\mathbf{k}$– can also be done as a matrix multiplication. In short, we can formulate both the evaluation and combination of the integrals in terms of procedures that are either perfectly parallel (involving no communication overhead) or highly efficient and relatively easy to program (multiplication of large, dense, distributed matrices). The remaining step, solving $\mathbf{A}\,\mathbf{x} = \mathbf{b}$ for $\mathbf{x}$, is straightforward.

The overall performance of our program on the *Intel Paragon* (512 processors) or *CRAY T3D* (256 processors) cannot be characterized by a single number. Although evaluating and subsequently combining the integrals are by far the dominant steps in the calculation, the relative importance of these two steps is strongly dependent on factors such as the size of the molecule and the number of inelastic channels (processes) being

considered. Depending on the nature of the calculation at hand and taking into account load balance, communication, I/O, and other overhead, we typically see throughput speeds in the range from 3 to 10 gigaflops. To put these numbers in perspective, our original sequential program, which is only partially vectorizable, averages about 30 megaflops on a Y-MP processor.

• This significant improvement in computational performance has greatly facilitated our efforts to obtain electron-collision cross sections for gases relevant to plasma processing in semiconductor fabrication, e.g., phosphine (PH_3), arsine (AsH_3), silane (SiH_4), tetrafluoromethane (CF_4), CHF_3, C_2F_6 and c-C_4F_8. We have also completed a project under the sponsorship of SEMATECH, Inc., to generate cross section sets for species relevant to boron trichloride ($BC\ell_3$) etching plasmas.

• We have also completed calculations of the elastic and momentum transfer cross sections for collisions of low-energy electrons with trimethylaluminum $(CH_3)_3$ $A\ell$. There is no electron collision data available for this species which is used in plasmas for deposition of aluminum nitride films and of aluminum metal on fibers for manufacture of fiber-reinforced composites, and for aluminum coating of the surface of ultra-fine particles. These results will also be used to put recent relative measured cross sections on an absolute scale.[3]

• In a joint effort with Professor Ehrhardt's group of Kaiserslautern University (Germany), we have carried out combined theoretical and experimental studies of the cross sections for electronic excitation of N_2 and CO by electron impact in the threshold region. Studies of such cross sections in the near-threshold region, which are often of greatest interest in simulations of weakly ionized plasmas, pose significant experimental and theoretical challenges. It is exactly in this region where available data is least reliable.

• We have completed extensive calcualtions of the cross sections for electron-impact excitation of the six lowest electronic states of CO_2 from their excitation thresholds to tens of electron volts above threshold. These studies provide the first estimates of these cross sections for CO_2. There have been very few measurements of these cross sections. These results are now being written up for publication.

• We continue to improve and extend our parallel computer codes for carrying out these calculations. One of the main computational tasks in these calculations is the evaluation of large numbers (trillions or more) of so-called two-electron repulsion integrals involving Cartesian Gaussians and plane wave functions. Improving the efficiency of the integral evaluation procedure can have a major impact on the speed of these calculations, which often run for hours on large parallel computers. In the past year, a completely new

set of subroutines for computing these integrals was written. A key feature of the new routines is that classes of related integrals are treated together, so that many intermediate quantities are computed only once for each class and reused. The new routines also incorporate a pre-screening technique based on rigourous upper bounds that are inexpensive to compute: Integrals that would be numerically zero are not computed at all. The combined effect of these two improvements is substantial. In fact, the new routines run from 3 to 5 or more times faster than the old routines.

- To date we have used large parallel computers such as the Cray T3D and Intel Pargon in our studies. These computers consist of hundreds of computational nodes connected by a high-speed communication network to one another and to peripheral devices such as disk storage. With the dramatic improvements in PC performance, a network of mass-market processors such as the 200 MHz Intel Pentium Pro. interconnected with 100 Mbits per second ethernet, producing several-hundred-megaflop or one gigaflop performance and dedicated exclusively to our work, is a suitable compute-engine for carrying out significant calcualtions of electron-collision cross sections. We have recently been awarded an equipment grant of $200,000 from Intel that will enable us to construct a substantial computer cluster of this kind that we will operate as a virtual parallel computer dedicated to our electron-molecule collision studies.

Publications

1. *Electronic Excitation of CH_4 by Electron Impact*
   C. Winstead, Q. Sun, V. McKoy, J.L.S. Lino, and M.A.P. Lima
   J. Chem. Phys. **98**, 2132 (1993)

2. *Studies of Electron-Molecule Collisions on Distributed-Memory Parallel Computers*
   P. Hipes, C. Winstead, Q. Sun, M.A.P. Lima, and V. McKoy
   Parallel Computing Works, eds. G.C. Fox, P. Messina, and R.D. Williams
   (Morgan-Kaufmann, San Mateo, 1994), pp. 320-331

3. *Electronic Excitation of Silane (SiH_4) by Low-Energy Electron Impact*
   C. Winstead, H. Pritchard, and V. McKoy
   J. Chem. Phys **101**, 338 (1994)

4. *Studies of Electron-Molecule Collisions on Massively Parallel Computers*
   C. Winstead and V. McKoy

Proceedings of the Mardi Gras '93 Conference on High-Performance Computing and its Applications in the Physical Sciences, eds. R. Kalia et al. (World Scientific, 1994), pp. 154-175

5. *Studies of Electron-Molecule Collisions on Massively Parallel Computers*
   C. Winstead and V. McKoy
   Modern Electronic Structure Theory
   Edited by D. Yarkony (World Scientific, 1995), pp. 1375-1462

6. *Electron-Molecule Collisions for Plasma Modelling: Experiences on the CRAY T3D*
   C. Winstead, H.P. Pritchard, and V. McKoy
   CRAY CHANNELS **17**, 10 (1995)

7. *Parallel Computation of Electron-Molecule Collisions*
   C. Winstead, H.P. Pritchard, and V. McKoy
   Computational Science and Engineering, Fall Issue, 34 (1995)

8. *Electron Scattering by Small Molecules*
   C. Winstead and V. McKoy
   Advances in Chemical Physics
   Edited by I. Prigogine and S.A. Rice (Wiley, 1996), Vol. 36, pp. 183-219.

9. *Absolute Cross Sections for Electron-Impact Excitation of CO Near-Threshold*
   J. Zobel, U. Mayer, K. Jung, H. Ehrhardt, H.P, Pritchard, C. Winstead, and V. McKoy
   J. Phys. B **29**, 839 (1996)

10. *Highly Parallel Computational Techniques for Electron-Molecule Collisions*
    C. Winstead and V. McKoy
    Advances in Atomic, Molecular and Optical Physics
    Edited by B. Bederson and H. Walther (Academic, 1996), Vol. 36, pp. 183-219

11. *Parallel Computing and The Generation of Basic Plasma Data*
    V. McKoy, C. Winstead, and C-H. Lee
    J. Vac. Sci. and Tech. A, January (1997).

12. *Collisions of Low-Energy Electrons with CO_2*
    C-H. Lee, C. Winstead, and V. McKoy
    J. Chem. Phys. (submitted)

Personnel Supported

Principal Investigator: Vincent McKoy, Professor of Chemistry

C-H. Lee, a graduate student, Evan Reed and Eric Liang, undergraduate students, are involved in this effort.

Interactions/Transitions

Presentations

- *Studies of Electron-Molecule Collisions on Highly Parallel Computers* , Invited Paper, 46th Gaseous Electronics Conference, Montreal, Quebec, October 1993.

- *Studies of Electron-Molecule Collisions on Parallel Computers*, Frontiers in Chemical Research Lecture, Texas A & M, December 1993.

- *Electron-Molecule Collisions for Modelling Materials-Processing Plasmas*, Invited Talk at Research Directors Conference, California Institute of Technology, February 1994.

- *Electron-Molecule Collisions for Modelling Materials-Processing Plasmas* , Invited Lecture at the Mardi Gras Conference: Towards Teraflop Computing, Louisiana State University, February 1994.

- *Electron-Molecule Collisions for Modelling Materials-Processing Plasmas*, Invited Talk at the High-Performance Computing Symposium of the International Simulation Multiconference, La Jolla, April 1994.

- *Studies of Electron-Molecule Collisions on Highly Parallel Computers*, Joint Chemistry-Mechanical Engineering Seminar, Ohio State University, May 1995.

- *Electron-Molecule Collision Calculations for Modelling of BCl_3 Plasmas*, Invited Talk at the IEEE International Conference on Plasma Science, Santa Fe, June 1994.

- *Data for Modelling Materials-Processing Plasmas: The Impact of Parallel Computers*, Invited Talk at the Symposium on Applications of Advanced Innovative Computational Methods to Defense Science and Engineering, Institute for Defense Analyses, November 1994.

- *Data for Modelling Materials-Processing Plasmas: The Impact of Parallel Computers*, Invited Talk in the High-Performance Computing Seminar Series, National Institute for Standards and Technology, Gaithersburg, April 1995.

- *Studies of Electron-Molecule Collisions on Highly Parallel Computers*, Seminar at the Geophysics Laboratory, Hanscom AFB, May 1995.

- *Studies of Electron-Molecule Collisions on Highly Parallel Computers*, Bucy Lecture, Texas Tech University, February 1995.

- *Studies of Electron-Molecule Collisions on Parallel Computers*, Invited Talk at the Annual Meeting of the Division of Atomic, Molecular and Optical Physics, American Physical Society, Toronto, May 1995.

- *Basic Data for Plasma Reactor Modelling: Exploiting Parallel Computers*, Invited Talk at the Mardi Gras '95 Conference on High-Performance Computing Technologies and Applications, Baton Rouge, February 1995.

- *High-Performance Simulation Tools for Microelectronics Fabrication*, Invited Talk at the Mardi Gras '96 Conference on Experimentala nd Simulation Challenges in Nanostructured Materials, Baton Rouge, LA, February 1996.

- *Some Developments in Simulations of Plasma Reactors*, Invited Talk at the Center for Cooperative Research in Advanced Science and Technology, Nagoya University, Nagoya (Japan), December 1995.

- *The Impact of Parallel Computers: Electron Collision Data for Plasma Modelling*, National Plasma Data Center, Nagoya (Japan), December 1995.

- *Studies of Electron-Molecule Collisions on Highly Parallel Computers*, Invited Talk at the Fourth Conference on Current Trends in Computational Chemistry, US Army Engineer Waterways Experiment Station, Vicksburg, MS, November, 1995.

- *Parallel Computing and The Generation of Basic Plasma Data*, Invited Talk at the International Workshop on Basic Aspects of Nonequilibrium Plasmas Interacting with Surfaces, Shirahama, Japan, January 1997.

- *Electron-Molecule Collisions For Plasma Modelling*, Invited talk at he Conference on Multiscale Phenomena in Science and Engineering, Louisiana State University, Baton Rouge, Louisiana, February 1997.

Advisory Function

Member, Wright Laboratory Board of Visitors; Independent Strategic Assessment Group (Col. Richard Davis), 1996.